Supplemental Table 1

Fragments detected in the ECD analysis shown in Figure 6.

$\text{Mass}_{\text{determined}}$ (singly charged)	Ion $_{\text{observed}}$	Assignment (Ac/Me$_3$; Ac$_2$/AcMe$_3$/Me$_6$) with $\text{Mass}_{\text{theoretical}}$	Δ[ppm]
356.2667	356.2667+	c_3+42 356.2298/<u>356.2661</u>	+ 1.6
484.3646	484.3646+	c_4+42 484.3248/<u>484.3612</u>	+ 7
526.3735	526.3735+	c_4+2x42 526.3354/<u>526.3718</u>/526.4082	+ 3
723.4889	723.4889+	c_7+42 723.4518/<u>723.4882</u>	+ 0.9
754.3535	754.3535+	z_7 754.3497	− 5
765.5049	765.5049+	c_7+2x42 765.4623/<u>765.4988</u>/765.5351	+ 8
794.5254	397.7666(2+)	c_8+42 794.4889/<u>794.5252</u>	+ 0.2
836.5386	418.7732(2+)	c_8+2x42 836.4995/<u>836.5358</u>/836.5721	+ 3.3
936.6012	468.8045(2+)	c_{10}+42 936.5631/<u>936.5995</u>	+ 1.8
1025.5023	1025.5023+	z_{10} 1025.5029	− 0.5
1065.6380	533.3229(2+)	c_{11}+42 1065.6066/<u>1065.642</u>	− 3.7
1107.6556	554.3317(2+)	c_{11}+2x42 1107.6171/<u>1107.6525</u>/1107.6889	+ 2.7
1167.6792	584.3435(2+)	*c_{11}+2x42 1167.6372/<u>1167.6736</u>/1167.71	+ 4.7
1193.7422	597.3750(2+)	c_{12}+42 1193.7006/<u>1193.737</u>	+ 4.3
1235.7426	618.3752(2+)	c_{12}+2x42 1235.7111/<u>1235.7475</u>/1235.7839	− 3.9
1253.7572	627.3825(2+)	*c_{12}+42 1253.7217/<u>1253.7581</u>	+ 0.7
1363.8462	682.4270(2+)	c_{13}+2x42 1363.806/<u>1363.8424</u>/1363.8788	+ 2.7

1548.9870	774.9974(2+)	c_{15}+42 1548.9589/<u>1548.9953</u>	− 5.3
1591.0198	796.0138(2+)	c_{15}+2x42 1590.9694/<u>1591.0058</u>/1591.0422	+ 8.7
1677.1072	839.0575(2+)	c_{16}+42 1677.0539/<u>1677.0903</u>	+ 10
1697.8420	849.4249(2+)	*z_{17} 1697.8472	+ 3
1711.8740	856.4409(2+)	z_{17} 1711.8628	+ 6.5
1719.0962	860.0520(2+)	c_{16}+2x42 1719.0644/<u>1719.1008</u>/1719.1372	− 2.6
1737.1144	869.0611(2+)	*c_{16}+42 1737.075/<u>1737.1114</u>	+1.7
1779.1298	890.0688(2+)	*c_{16}+2x42 1779.0855/<u>1779.1219</u>/1779.1583	+ 4.4
1848.9062	924.9570(2+)	z_{18} 1848.9218	− 8.4
1902.2206	951.6142(2+)	a_{19}+1+42 1902.1778/<u>1902.2142</u>	+ 3.3
1944.2304	972.6191(2+)	a_{19}+1+2x42 1944.1883/<u>1944.2247</u>/1944.2611	+ 2.9
1946.2225	649.4127(3+)	c_{19}+42 1946.1914/<u>1946.2278</u>	− 2.7
1988.2530	994.6304(2+)	c_{19}+2x42 1988.2019/<u>1988.2383</u>/1988.2747	+ 7.3
2047.2766	683.0974(3+)	c_{20}+42 2047.2391/<u>2047.2755</u>	+ 0.5
2089.2904	697.1020(3+)	c_{20}+2x42 2089.2495/<u>2089.2859</u>/2089.3224	− 2.1
2176.3306	726.1154(3+)	c_{21}+42 2176.2817/<u>2176.3181</u>	+ 5.7
2236.3522	746.1226(3+)	*c_{21}+42 2236.3028/<u>2236.3392</u>	+ 5.8
2304.4204	768.8120(3+)	c_{22}+42 2304.3767/<u>2304.4131</u>	+ 3.1
2345.4316	782.4824(3+)	c_{22}+2x42 2346.3872/<u>2346.4236</u>/2346.46	+ 3.4
2364.4396	788.8184(3+)	*c_{22}+42 2364.3978/<u>2364.4342</u>	+ 2.2
2432.5240	811.5132(3+)	c_{23}+42 2492.4928/<u>2492.5292</u>	− 2
2474.5321	825.5159(3+)	c_{23}+2x42 2534.5033/<u>2534.5397</u>/2534.5761	− 2.9
2546.5525	849.5227(3+)	c_{24}+42 2546.5146/<u>2546.551</u>	+ 0.5
2585.3554	1293.1816(2+)	z_{25} 2585.3449	+ 4
2588.5626	647.8965(4+)	c_{24}+2x42 2588.5251/<u>2588.5615</u>/2588.5979	+ 0.4
2802.7597	934.9251(3+)	c_{26}+42 2802.7045/<u>2802.7409</u>	+ 6.7
2844.7522	711.9439(4+)	c_{26}+2x42 2844.715/<u>2844.7514</u>/2844.7878	+ 0.2
2930.8394	733.4657(4+)	c_{27}+42 2930.7994/<u>2930.8358</u>	+ 1.2

2972.8561	991.6239(3+)	c_{27}+2x42 2972.8099/<u>2972.8463</u>/2972.8827	+ 3.2
3086.9044	1029.6400(3+)	c_{28}+42 <u>3086.9006</u>/3086.937	+ 1.2
3173.9786	794.2505(4+)	c_{29}+42 3173.9326/<u>3173.969</u>	+ 3
3215.9562	804.7449(4+)	c_{29}+2x42 <u>3215.9431</u>/3215.9795/3216.0159	+ 4
3303.0274	826.5127(4+)	c_{30}+42 3302.9753/<u>3303.0116</u>	+ 4.4
3345.0193	1115.6783(3+)	c_{30}+2x42 3344.9858/<u>3345.0222</u>/3345.0586	− 0.8
3551.1383	711.0339(5+)	c_{32}+42 3551.0913/<u>3551.1227</u>	− 4.3
3565.9540	1189.3232(3+)	z_{34} 3566.9308	+ 6.5
3593.1098	719.4282(5+)	c_{32}+2x42 <u>3593.1018</u>/3593.1382/3593.1746	+2.2
3611.1558	723.0374(5+)	*c_{32}+42 3611.1124/<u>3611.1488</u>	+ 1.9
3653.1358	731.4334(5+)	*c_{32}+2x42 <u>3653.1229</u>/3653.1593/3653.1957	+ 3.5
3810.0787	1270.6981(3+)	z_{36} 3810.0640	+ 3.8
3883.0975	1295.0377(3+)	*z_{37} 3883.0803	+ 4.4
3897.0847	1299.7001(3+)	z_{37} 3897.0960	− 2.8
4111.2379	1371.0845(3+)	z_{39} 4111.2277	+ 2.4
4158.4578	832.4978(5+)	c_{37}+42 4158.4282/<u>4158.4646</u>	− 1.6
4200.4998	840.9062(5+)	c_{37}+2x42 4200.4387/<u>4200.4751</u>/4200.5115	+ 5.8
4218.4553	844.4973(5+)	*c_{37}+42 <u>4218.4494</u>/4218.4858	+ 1.3
4242.5158	1061.3848(4+)	a_{38}+1+42 <u>4242.5095</u>/4242.5459	+ 1.4
4267.3765	1423.1307(3+)	z_{40} 4267.3288	+ 11
4284.5642	857.7191(5+)	a_{38}+1+2x42 4284.52/<u>4284.5564</u>/4284.5928	+ 1.8
4651.5890	1163.6531(4+)	*z_{43} 4651.589	0
4812.5754	1203.8997(4+)	z_{44} 4812.6362	− 12.6
5088.0693	1018.4201(5+)	c_{45}+42 5088.0093/<u>5088.0457</u>	+ 4.6
5130.0648	1026.8192(5+)	c_{45}+2x42 5130.0198/<u>5130.0562</u>/5130.0926	+ 1.6
5302.1010	1326.2811(4+)	c_{47}+42 <u>5302.1047</u>/5302.1411	− 0.6
5344.1752	891.5357(6+)	c_{47}+2x42 5344.1152/5344.1516/<u>5344.188</u>	− 2.3
5643.3574	941.3994(6+)	a_{51}+1+42 5643.3235/<u>5643.3599</u>	− 0.4

6017.5450	1003.7640(6+)	c_{54}+42 6017.5098/<u>6017.5462</u>	− 0.1
6428.4646	1607.8720(4+)	z_{58} 6428.5408	− 12
6917.7328	1153.7953(6+)	z_{62} 6917.7632	− 4.3
7823.1550	1304.6990(6+)	z_{70}(ox) 7823.1731	− 2.3
8192.2774	1366.2194(6+)	z_{74} 8192.4107	− 16
8406.5848	1401.9373(6+)	z_{76} 8406.5061	+ 9.3
8626.4956	1438.5891(6+)	*z_{78} 8626.6021	− 12.3
8755.6936	1460.1221(6+)	z_{79}(ox) 8755.681	+ 1.4
8828.9668	1262.1448(7+)	c_{78}+42 8828.9475/<u>8828.9839</u>	− 1.9
8870.9213	1268.1383(7+)	c_{78}+2x42 <u>8870.958</u>/8870.9944/8871.0308	− 4.1
8931.0275	1276.7249(7+)	*c_{78}+2x42 8930.9792/<u>8931.0156</u>/8931.052	+ 1.3
9223.8652	1538.1507(6+)	z_{83}(ox) 9223.9871	− 13
9336.1147	1334.5945(7+)	z_{84} 9336.0871	+ 2.9
9383.2622	1173.7896(8+)	c_{82}+42 <u>9383.2877</u>/9383.3241	− 2.7
9684.3094	1211.4205(8+)	c_{85}+42 <u>9684.4514</u>/9684.4878	− 14.6
10563.767	1174.6471(9+)	z_{94} 10563.7159	+ 4.8
10691.676	1337.3407(8+)	z_{95} 10691.8109	− 12.6
11548.262	1284.0360(9+)	z_{102} 11548.324	− 5.3

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- The +42 Da modification may represent acetylation or trimethylation. Masses calculated are listed in this order. The underlined mass is closer to the mass observed and the deviation is calculated for this one.

- The +84 Da modification may represent two acetyl groups, the combination of acetylation and trimethylation, or double trimethylation. The calculated masses are listed in this order. The underlined mass is the closest to the mass observed and the deviation is calculated for this one.

- Some fragments were represented by ions of multiple charge states, only one of them is listed.

- Precursor ions, and neutral losses from precursor ion are not listed here.

- Peak mass accuracies are sometimes sub-optimal due to poor ion statistics caused by low peak intensities.

Supplemental Table 2

CID data of AP**KK**(Ac, Me₃)APAAAA acquired by the QSTAR Pulsar instrument

Mass$_{determined}$	Ion$^{2+}_{observed}$	Assignment	Mass$_{calculated}$(Ac₂/AcMe₃/Me₆)[a]	Δ [ppm]
70.0676		P	70.0657	+27
115.0867		AA-28	115.0871	-3
126.0925		K(Ac)	126.0919	+27
141.1077		a₂/AP-28/PA-28	141.1028	+35
143.0843		AA	143.0821	+15
161.0948		y₂	161.0926	+14
169.1013		b₂/PA/AP	169.0977	+21
232.1331		y₃	232.1297	+15
240.1382		PAA/APA	240.1348	+14
311.1808		PAAA/APAA	311.1719	+19
509.3554		b₄/PK*K*A/K*K*AP[b]	509.3088/<u>509.3452</u>/509.3816	+20
535.3772	268.1925	a₅-NH₃	535.3244/<u>535.3608</u>/535.3972	+31
552.3975		a₅/K*K*APA-28	552.3510/<u>552.3874</u>/552.4238	+18
552.3929	276.7004	as above	as above	+10
578.4262	289.7170	PK*K*AP-28	578.3666/578.403/<u>578.4394</u>	-23
580.3822		b₅//K*K*APA	580.3459/<u>580.3823</u>/580.4138	-0.1
580.3968	290.7023	as above	as above	+25
606.3904		PK*K*AP	606.3615/<u>606.3979</u>/606.4343	-12

606.4089	203.7079	as above	as above	+17
623.4134		K*K*APAA-28	623.3881/<u>623.4245</u>/623.4609	-18
623.4418	312.2248	as above	as above	+28
649.4450	325.2264	a_6/PK*K*APA-28	649.4037/<u>649.4401</u>/649.4765	+8
651.4081		K*K*APAA	651.3830/<u>651.4194</u>/651.4558	-17
651.4292	326.2185	as above	as above	+15
677.4436	339.2257	b_6/PK*K*APA	677.3986/<u>677.435</u>/677.4714	+13
720.4550	360.7314	a_7/ PK*K*APAA-28	<u>720.4408</u>/720.4772/720.5136	+20
748.4628	374.7353	b_7/ PK*K*APAA	748.4357/<u>748.4721</u>/748.5058	-12
774.4746	387.7412	a_8-NH_3	774.4514/<u>774.4878</u>/774.5242	-17
791.5098	396.2588	a_8/ PK*K*APAAA-28	791.4779/<u>791.5143</u>/791.5507	-6
819.5088	410.2583	b_8/ PK*K*APAAA	819.4729/<u>819.5093</u>/819.5457	-0.4
862.5548	431.7813	a_9	862.5151/<u>862.5515</u>/862.5879	+4
890.5516	445.7797	b_9	890.5100/<u>890.5464</u>/890.5828	+6

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[a] the +84 Da modification may represent two acetyl groups, the combination of acetylation and trimethylation, or double trimethylation. The calculated masses are listed in this order. The underlined mass is the closest to the mass observed and the deviation is calculated for this one.

[b] some sequence ions and internal fragments have identical amino acid compositions